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CO₂ MITIGATION VIA ACCELERATED LIMESTONE WEATHERING

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April 16, 2004

American Chemical Society National Meeting
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CO₂ MITIGATION VIA ACCELERATED LIMESTONE WEATHERING

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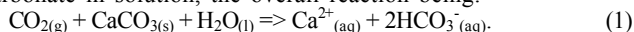
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Introduction

The climate and environmental impacts of our current, carbon-intensive energy usage demands that effective and practical energy alternatives and CO₂ mitigation strategies be found.^{1,2} As part of this effort, various means of capturing and storing CO₂ generated from fossil-fuel-based energy production are being investigated.³ One of the proposed methods involves a geochemistry-based capture and sequestration process^{4,5} that hydrates point-source, waste CO₂ with water to produce a carbonic acid solution. This in turn is reacted and neutralized with limestone, thus converting the original CO₂ gas to calcium bicarbonate in solution, the overall reaction being:



The dissolved calcium bicarbonate produced is then released and diluted in the ocean where it would add minimally to the large, benign pool of these ions already present in seawater.

Such a process is geochemically equivalent to continental and marine carbonate weathering which can otherwise naturally consume most anthropogenic CO₂, but over many millennia.⁶⁻⁸ We identify the enhanced form of this process as Accelerated Weathering of Limestone or AWL. Previously, it has been shown that AWL can effectively convert a significant fraction of US CO₂ emissions to long-term storage as bicarbonate in the ocean, while avoiding or possibly reversing environmental impacts associated with either the ongoing passive or the proposed active injection of CO₂ into the ocean.^{5,9} Being analogous to the wide-spread use of wet limestone to desulfurize flue gas, AWL reactors could be retrofitted to many existing coastal power plants at a typical cost estimated to be \$20-\$30/tonne CO₂ mitigated.^{4,10}

Limestone and Seawater Availability and Cost

Based on reaction 1, it would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react 1 tonne of CO₂ to form 2.8 tonnes of HCO₃⁻ in solution. It is envisioned that abundant and inexpensive limestone (containing 92-98% CaCO₃) would be used. US production of this mineral is presently 10⁹ tonnes/yr, with reserves sufficient to satisfy US demand for many decades if not centuries. Channeling the entire yearly US limestone production to AWL could consume roughly 18% of the annual CO₂ generated by electricity production in the US.

However, currently more than 20% of US limestone production and processing results in waste limestone fines (<10 mm) that have little or no market value and are accumulating at limestone mining and processing sites.^{11,12} This suggests that a sizeable, free or low-cost source of limestone could be available for AWL whose use could also help alleviate the significant limestone waste problem.

Because of the significant quantities of water required to react the CO₂ and to carry and dilute the resulting bicarbonate (>10⁴ tonnes H₂O/tonne CO₂; ref. 4), AWL reactors in close proximity to seawater would be at a distinct advantage. About 12% of CO₂ emissions from US electricity production occurs at plants within 10 km of the US coastline.¹⁰ Fortuitously, the

majority of this coastline is also within 400 km of known limestone reserves.¹³ This is especially true of the southern and eastern seaboard that also has the highest density of coastal US power plants and coastal electricity-related CO₂ production. For example there is more than 20 GW of fossil-fueled power generation (≈100 billion tonnes CO₂ emitted/yr) by coastal power plants in Florida¹⁰, a state that is almost entirely underlain by carbonate deposits.¹⁴

In such ideal settings, if both limestone and its transportation costs were negligible, the CO₂ mitigation cost offered by AWL could be \$3 - \$4/tonne CO₂ based on previous cost analyses.^{4,10} This would especially pertain if the hundreds of millions of gallons of seawater already pumped and used for cooling by these plants each day were in turn used as a “free” AWL water source. This cost is significantly lower than most other current or proposed abiotic technologies.³ However, the number of ideal sites and hence the volume of CO₂ that could be treated at this very attractive cost would be small. Considering water, limestone, and transportation cost in more typical coastal settings suggests that 10-20% of US energy CO₂ emissions could be mitigated at \$20-\$30/tonne. This is still very cost-competitive with other methods, especially considering that the cost of conventional amine CO₂ capture (not required for AWL) is generally >\$30/tonne CO₂ (ref. 15).

The preceding assumes an AWL reactor sited at the source of waste CO₂ (i.e. a power plant) and to which limestone and seawater are transported. Alternatively, CO₂ generated at inland locations could be transported to coastal AWL reactors sited at or near limestone quarries. Transport of CO₂ is inexpensive (\$0.06 tonne⁻¹ km⁻¹, ref. 16) relative to the cost of transporting the AWL-equivalent (2.5 tonnes) of limestone. However, this would require initial CO₂ separation, capture, and liquefaction, with the associated technology and energy costs that are presently significant, as mentioned above. Still, if inexpensive CO₂ capture/separation is developed, piping CO₂ to coastal AWL reactors could prove cost-competitive with other forms of CO₂ sequestration such as underground storage, especially in regions where the underlying geology is not amenable to CO₂ retention.

Reaction Rates and Densities

The results of experiments in our laboratory yielded limestone dissolution rates ranging from roughly 10⁻⁷ to 10⁻⁵ mols m⁻² s⁻¹ with positive sensitivity to flow rate, stir rate, and CO₂ concentration. Dissolution rates in seawater were equal to or higher than those in distilled water under otherwise identical conditions.

Assuming a reaction rate of 10⁻⁶ mols m⁻² s⁻¹ is achievable in large-scale reactors, a bed of 1mm-diameter limestone particles (typical of waste limestone fines discussed above) yields an surface area/volume of ≥4.4 x 10³ m²/m³. Therefore a maximum of 60 m³ of such limestone particles would be needed to react 1 tonne of CO₂ per day. For a cubic reactor volume (roughly 4m x 4m x 4m), this equates to an areal reaction rate of at least 15 tonnes CO₂ m⁻² day⁻¹, or about a million times greater than optimum biotic CO₂ uptake and sequestration rates.¹⁶ The experiments suggest that this density of CO₂ conversion to HCO₃⁻ could be increased by as much as an order of magnitude by increasing stirring and flushing rate, though at added energy and cost penalties.

Effectiveness

Using a box model of ocean chemistry and transport Caldeira and Rau⁵ showed that the release of the bicarbonate-charged effluent from carbonate dissolution would more effectively sequester CO₂ over the long term relative to direct CO₂ injection

at equivalent ocean depths. This has been subsequently confirmed for releases at several different ocean locations and depths in a 3-D ocean general circulation model (**Figure 1**). Injection of pure CO₂ at great depth in the ocean effectively stores most of the injected carbon for hundreds of years or more.⁵ Therefore, the additional slowing of CO₂ leakage that would be gained by releasing carbonate dissolution effluent at the same depth may not be economically significant. Nevertheless, we note that carbonate dissolution can make a major contribution for less costly shallow-water releases and greatly improves effectiveness of long-term ocean carbon sequestration regardless of the depth at which the effluent is released.

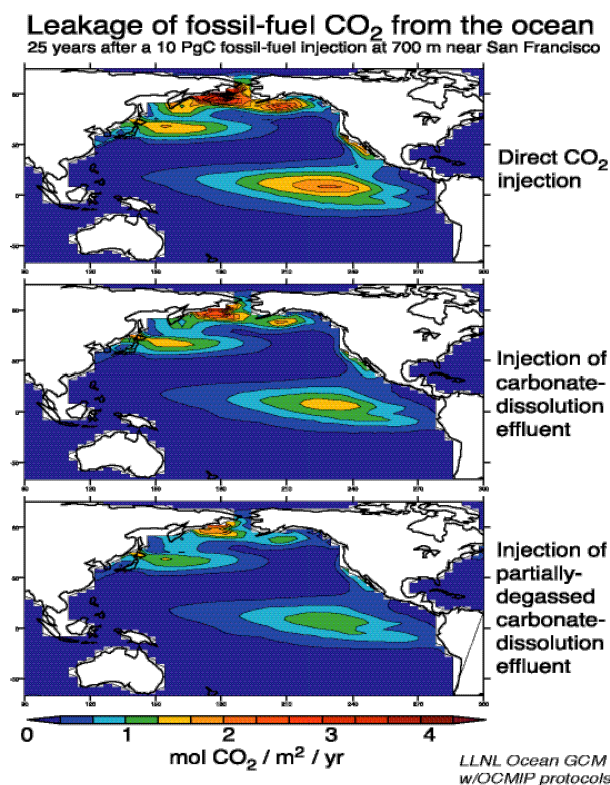


Figure 1. Ocean general circulation model results showing the greater effectiveness (less CO₂ leakage to atmosphere) inherent in the injection of carbonate dissolution effluent as compared to molecular CO₂ at equivalent depths.

Environmental Impacts/Benefits

An increase in ocean acidity (reduction in pH) is a serious environmental issue caused either by the ongoing diffusive uptake of anthropogenic CO₂ from the atmosphere or the proposed purposeful injection of CO₂ into the ocean.⁹ Storing waste CO₂ in the form of bicarbonate ions balanced by Ca²⁺ rather than H⁺ (i.e., as carbonic acid) substantially lessens the increase in acidity per tone of carbon added to the ocean, while reducing harmful effects to marine biota of direct ocean CO₂ additions.^{17,18} In fact, Ca²⁺ and bicarbonate enrichment of seawater has been shown to significantly enhance the calcification and growth rate of marine corals.^{19,20}

Nevertheless, negative marine environmental impacts could result via reduction in oxygen concentration in the effluent through partial equilibration with flue-gas streams. As well, impurities released into the effluent solution from the limestone or the flue gas could be biotically impactful. Experimentation is required to quantify such effects. We point out, however, that the

ocean naturally receives and accommodates about 2 x 10⁹ tonnes of dissolved calcium bicarbonate per year produced from continental carbonate weathering as delivered by rivers.²¹

We also note that limestone is already widely used for environmental benefit, flue gas desulfurization and acid mine waste neutralization being prime examples.

Conclusions

In the appropriate settings AWL is an attractive option for CO₂ mitigation because: 1) the required reactants are relatively inexpensive, abundant, and environmentally benign, 2) the technology is relatively simple, low-cost, and amenable to power plant retrofitting, even in developing countries, 3) the storage is effective and long-term, and 4) the waste products are stable and appear to have net positive environmental benefit. All of these features derive from the fact that AWL merely enhances Nature's own CO₂ mitigation mechanism, carbonate weathering. More research is needed, however, to more accurately assess the costs, benefits, and impacts of this means of mitigating CO₂ from point sources.

References

- (1) Houghton J. *Global warming: The complete briefing*. Cambridge: Cambridge, 1997.
- (2) Hoffert, M. I.; Caldeira, K.; Benford, G.; Criswell, D. R.; Green, C.; Herzog, H.; Jain, A. K.; Kheshgi, H. S.; Lackner, K. S.; Lewis, J. S.; Lightfoot, H. D.; Manheimer, W.; Mankins, J. C.; Mauel, M. E.; Perkins, L. J.; Schlesinger, M. E.; Volk, T.; Wigley, T. M. L., *Science*, **2002**, 298, 981-987.
- (3) D.O.E. *Carbon sequestration project portfolio FY 2002*. NETL and Office of Fossil Energy, U.S. Department of Energy, Wash., D.C., 2003.
- (4) Rau, G. H.; Caldeira, K., *Energy Convers. Manag.*, **1999**, 40, 1803-1813.
- (5) Caldeira, K.; Rau, G. H., *Geophys. Res. Lett.*, **2000**, 27, 225-228.
- (6) Sundquist, E. T., *Quatern. Sci. Rev.*, **1991**, 10, 283-296.
- (7) Murray C. N.; Wilson T. R. S., *Energy Convers. Manag.*, **1997**, 38, S287-S294.
- (8) Archer, D.; Kheshgi, H.; Maier-Reimer, E., *Geophys. Res. Lett.*, **1997**, 24, 405-408.
- (9) Caldeira, K.; Wickett, M. E., *Science* **2003**, 425, 365.
- (10) Sarv H.; Downs, W., *CO₂ capture and sequestration using a novel limestone lagoon scrubber - A white paper*, McDermott Technology, Inc, Alliance, OH, 2002.
- (11) Hudson, W. R.; Little, D.; Razmi, A. M.; Anderson, V.; Weissmann, A., *An investigation of the status of by-product fines in the United States*. International Center for Aggregates Res. Report ICAR-101-1, 1997.
- (12) McClellan, G. H.; Eades, J. L.; Fountain, K. B.; Kirk, P.; Rothfuf, C., *Research and techno-economic evaluation: Uses of limestone byproducts*. University of Florida Department of Geological Sciences Final Report for Florida Department of Transportation Contract No. BA589, WPI 0510798, 2002.
- (13) Langer, W. H., *Natural aggregates of the conterminous United States*, U.S. Geological Survey Bulletin 1594, 1988.
- (14) Scott, T. M.; Campbell, K. M.; Rupert, F. R.; Arthur, J. D.; Missimer, T. M.; Lloyd, J. M.; Yon, J. W.; Duncan, J. G., *Geologic map of the State of Florida*. Florida Geol. Survey Map Series 146, Scale 1:750,000, 2001.
- (15) Rao, A. B.; Rubin, E. S., *Environ. Sci. Technol.*, **2002**, 36, 4467-4475.
- (16) D.O.E., *Carbon sequestration research and development*. Office of Science and Office of Fossil Energy, U.S. Department of Energy, Wash., D.C., 1999.
- (17) Caulfield, J. A.; Auerbach, D. I.; Adams, E. E.; Herzog, H. J., *Energy Convers. Manag.*, **1997**, 38, S343-S348.
- (18) Tamburri, M. N.; Peltzer, E. T.; Friederich G. E.; Aya, I.; Yamane, K.; Brewer, P. G., *Mar. Chemistry*, **2000**, 72, 95-101.
- (19) Marubini, F.; Thake, B., *Limnol. Oceanogr.*, **1999**, 44, 716-720.
- (20) Langdon, C.; Takahashi, T.; Sweeney, C.; Chipman, D.; Goddard, J.; Marubini, F.; Aceves, H.; Barnett, H.; Atkinson, M. J., *Glob. Biogeochem. Cycles*, **2000**, 14, 639-654.
- (21) Morse, J. W.; Mackenzie, F. T., *Geochemistry of Sedimentary Carbonates*, Elsevier: Amsterdam, 1990.